PB84-172097

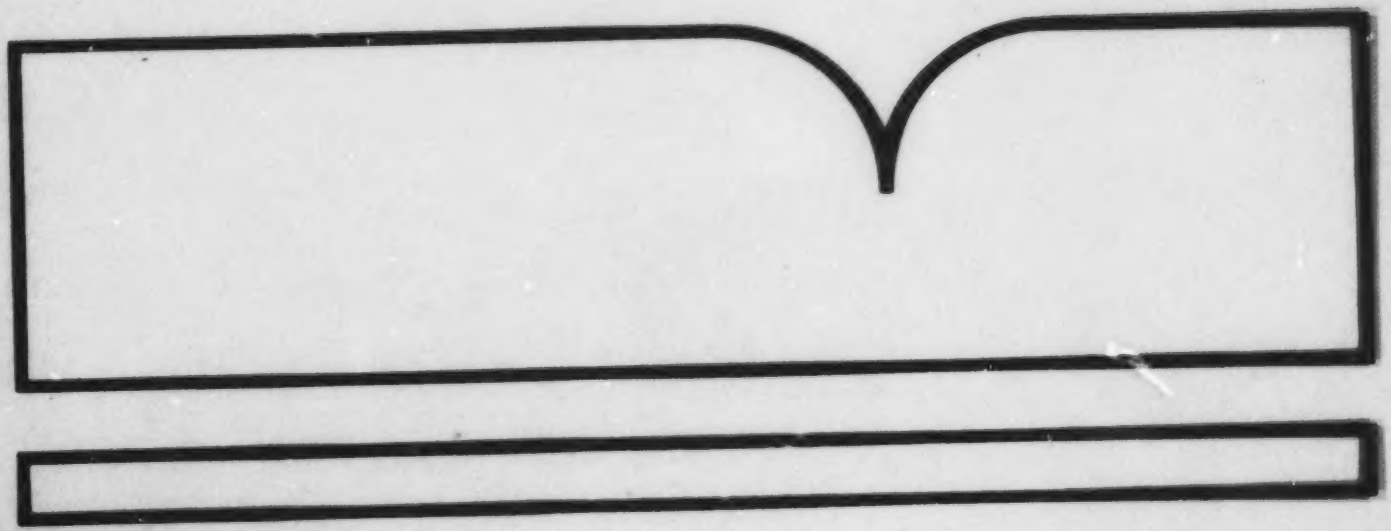
New Audit Method for EPA (Environmental Protection Agency) Reference Method 6

Research Triangle Inst.
Research Triangle Park, NC

Prepared for

Environmental Monitoring Systems Lab.
Research Triangle Park, NC

Mar 84



U.S. Department of Commerce
National Technical Information Service
NTIS

PB84-172097

EPA-600/4-84-025
March 1984

A NEW AUDIT METHOD FOR EPA REFERENCE METHOD 6

by

R.K.M. Jayanty
Research Triangle Institute
Post Office Box 12194
Research Triangle Park, NC 27709

EPA Contract No. 68-02-3767

RTI Task No. 43U-2474-11

EPA Task Manager
Robert G. Fuerst

Prepared for

U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Quality Assurance Division
Research Triangle Park, NC 27711

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/4-84-025		PB84 172092

4. TITLE AND SUBTITLE	5. REPORT DATE
A NEW AUDIT METHOD FOR EPA REFERENCE METHOD 6	March 1984
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
R. K. M. Jayanty	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Research Triangle Institute P.O. Box 12194 Research Triangle Park, NC 27709	11. CONTRACT/GRANT NO. 68-02-3767
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Monitoring Systems Laboratory Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, NC 27711	13. TYPE OF REPORT AND PERIOD COVERED Final 14. SPONSORING AGENCY CODE EPA 600/08

15. SUPPLEMENTARY NOTES

ORD Project Report

16. ABSTRACT

A simple, inexpensive, accurate method for evaluating and/or auditing sampling and analytical phases of the EPA Source Reference Method 6 was developed. The method uses a known amount of a chemical compound in the form of a tablet or pill (or placed in a capsule) to generate sulfur dioxide (SO_2) quantitatively by reaction with an acid. The reaction takes place in a compact glass impinger system that can be taken to the field. The SO_2 generated in test runs was collected and analyzed using the EPA Method 6 procedure. The SO_2 generation was quantitative and recoveries were 94 $\pm$ 5 percent. The time to complete the reaction was less than 15 min at a flow rate of 1 L/min, but the recommended sampling time was 45 min. The tablets prepared gravimetrically were found to be stable over a 6-month period. The between-laboratory results obtained showed close agreement with the expected concentrations, based on calculations from the stoichiometric reaction. The estimates of repeatability (or within-laboratory precision) were $\pm$ 5.0 mg 95 percent of the time for both concentration levels tested. The reproducibility (or between-laboratory precision estimate) was within $\pm$ 5.9 mg at the low range and $\pm$ 23.8 mg at the high range about 95 percent of the time. The maximum bias observed for the method was 0.5 percent.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	47
	20. SECURITY CLASS *(This page)*	22. PRICE
	UNCLASSIFIED	

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

DISCLAIMER

The information in this document has been funded wholly or in part by the U.S. Environmental Protection Agency under Contract No. 68-02-3767 to Research Triangle Institute. It has been subjected to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

Measurement and monitoring research efforts are designed to anticipate potential environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, has responsibility for: asessment of environmental monitoring technology and systems; implementation of Agency-wide quality assurance programs for air pollution measurement systems; and supplying technical support to other groups in the Agency including the Office of Air, Noise, and Radiation, the Office of Toxic Substances, and the Office of Enforcement.

The objective of this study was to investigate the development of a new performance audit procedure for EPA Source Reference Method 6 for sulfur dioxide. Currently, Method 6 audits conducted by EPA evaluate only the analytical phase. This report describes an audit procedure that evaluates both the sampling and the analytical phases of the method. The results of collaborative tests using the new audit procedure are also reported.

Thomas R. Hauser, Ph.D.
Director
Environmental Monitoring Systems Laboratory
Research Triangle Park, North Carolina

ABSTRACT

A simple, inexpensive, accurate method for evaluating and/or auditing sampling and analytical phases of the EPA Source Reference Method 6 was developed. The method uses a known amount of a chemical compound in the form of a tablet or pill (or placed in a capsule) to generate sulfur dioxide (SO_2) quantitatively by reaction with an acid. The reaction takes place in a compact glass impinger system that can be taken to the field. The SO_2 generated in test runs was collected and analyzed using the EPA Method 6 procedure. The SO_2 generation was quantitative and recoveries were 94 ± 5 percent. The time to complete the reaction was less than 15 min at a flow rate of 1 L/min, but the recommended sampling time was 45 min. The tablets prepared gravimetrically were found to be stable over a 6-month period. The between-laboratory results obtained showed close agreement with the expected concentrations, based on calculations from the stoichiometric reaction. The estimates of repeatability (or within-laboratory precision) were ±5.0 mg 95 percent of the time for both concentration levels tested. The reproducibility (or between-laboratory precision estimate) was within ±5.9 mg at the low range and ±23.8 mg at the high range about 95 percent of the time. The maximum bias observed for the method was 0.5 percent.

CONTENTS

Section		Page
Foreword		iii
Abstract		iv
Figures and Tables		vi
Acknowledgments		vii
1	Introduction	1
2	Summary and Conclusions	2
3	Development of an Audit Material	4
	Objectives	4
	Audit Method Selection	4
	Gas Cylinder Method	4
	Permeation Tube Method	5
	Thermal Decomposition Method	5
	Chemical Reaction Method	5
	Laboratory Evaluation	6
	Thermal Decomposition of Solids	6
	Chemical Reactions	7
	Audit Method Evaluation	10
	Preparation of Tablets	10
	Sampling and Analysis Procedures	10
	Results and Discussion	12
	Stability Study	12
4	Collaborative Testing	15
	Collaborative Test Design	15
	Interlaboratory Analysis Results	16
	Statistical Analysis	16
References		21
Appendix A.	Determination of Sulfur Dioxide Emissions From Stationary Sources - Method 6	A-1
Appendix B.	Outline of Method 6 Audit Procedure	B-1

FIGURES

Number		Page
1	Preliminary SO_2 generation system	8
2	Sampling train with SO_2 generator	11

TABLES

Number		Page
1	Tedlar Bag Results	9
2	Results of SO_2 Generated from the Prepared Tablets	13
3	Stability Study Results	14
4	Interlaboratory Analysis Results	17
5	Statistical Analysis Results	19

ACKNOWLEDGMENTS

This project was conducted by the Research Triangle Institute, Research Triangle Park, North Carolina, under Contract No. 68-02-3767 for the Quality Assurance Division, Environmental Monitoring Systems Laboratory, of the U.S. Environmental Protection Agency (EPA). The support of EPA and the guidance of the Task Manager, Robert G. Fuerst, are gratefully acknowledged.

Special acknowledgment is made to Mr. Thomas J. Logan and Mr. M. R. Midgett of EPA for their suggestions. Also, thanks are due to Mr. Jack C. Suggs of EPA for statistical analysis of the data and to Dr. W. F. Gutknecht, Dr. C. Eaton, Mr. R. Shores, Mr. L. Williams, and Ms. Ann Turner of Research Triangle Institute for technical advice and analytical support.

Special acknowledgment is also made to the concerned staffs at PEDCo Environmental, Incorporated, Engineering Science Incorporated, Entropy Environmentalists Incorporated, Radian Corporation, TRC-Environmental Consultants Incorporated, and TRW-Environmental Engineering Division for their participation in the collaborative testing program.

SECTION 1
INTRODUCTION

The U.S. Environmental Protection Agency (EPA) is interested in developing audit materials for all EPA source reference methods. These audit materials will be used to conduct performance audits during stationary source measurements. EPA currently provides liquid sulfate standards as audit materials for EPA Source Reference Method 6, which is used to determine sulfur dioxide (SO_2) emissions from stationary sources. However, these liquid sulfate audit standards are useful only for evaluating the analytical phase of EPA Method 6. Currently, sampling phase procedures are evaluated only by a systems audit; i.e., someone observing the sampling procedures in the field. Therefore, a method or device that can be used as an audit material for the evaluation of both the sampling and analytical phases of the source reference methods is needed.

Research Triangle Institute (RTI) was contracted by the Quality Assurance Division of EPA's Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, to develop a simple method or device for evaluating/auditing both the sampling and analytical phases of EPA Method 6. RTI selected an approach for the development of a simple audit method or device, developed a method, and conducted an interlaboratory and intralaboratory evaluation. The audit method was tested by six laboratories. This report summarizes the various activities performed during the study and includes: a summary of the study and descriptions of the different approaches for the development of an audit method or device for EPA Method 6, the evaluation of the selected method in the laboratory, and the collaborative testing procedure and analysis results.

SECTION 2
SUMMARY AND CONCLUSIONS

A simple, inexpensive audit method was developed for evaluating the sampling and analytical phases of EPA Method 6. The audit method uses a known amount of a chemical compound (sodium bisulfite or sodium sulfite) mixed with an inert binder (polyvinyl pyrollidine) and formed into a tablet or pill so that SO_2 is generated quantitatively by reaction with sulfuric acid. The SO_2 generated in test runs was collected and analyzed using the EPA Method 6 procedure. The SO_2 generation was quantitative and recoveries were 94 ± 5 percent over the 10- to 800-mg range of sodium bisulfite. The complete reaction was less than 15 min, at a flow rate of 1 L/min, but a 45-min sampling time was used. The prepared tablets were stable during a 6-month period.

The method was evaluated at two concentration levels at six laboratories to determine its repeatability, reproducibility, and accuracy. The interlaboratory results agreed well with the expected concentrations, which were based on calculations from the stoichiometric reaction. For the two concentration levels, the estimate of repeatability within a laboratory was found to be within ±5.0 mg 95 percent of the time. The estimate of reproducibility between laboratories was within ±5.9 mg at the low concentration and ±23.8 mg at the high concentration 95 percent of the time. The maximum bias observed was 0.5 percent by comparison with the expected concentrations. The SO_2 generation from the material was found to be independent of flow rate, total volume, and concentration of sulfuric acid. The amount of sulfuric acid must be slightly in excess of the amount required for the chemical reaction. Ten milliliters of 10-percent sulfuric acid was sufficient for the two concentration levels tested.

In summary, the intralaboratory and interlaboratory results showed that this method is viable for auditing sampling and analytical phases of EPA Method 6 in the field. A performance audit using this new audit method

for EPA Method 6 is recommended as a routine quality assurance (QA) procedure for future source SO_2 emissions analyses.

SECTION 3
DEVELOPMENT OF AN AUDIT MATERIAL

OBJECTIVES

The main objectives of this project were:

- To develop a simple method or device for auditing the sampling and analytical phases of EPA Reference Method 6
- To conduct collaborative testing to establish the accuracy and precision of the developed method or device
- To determine the stability of the audit material or device.

AUDIT METHOD SELECTION

Several methods can be used to generate standard atmospheres of sulfur dioxide. These methods include use of:

- Commercially available gas cylinders that contain known blends of SO_2 in an inert balance gas
- Permeation tube devices that contain SO_2
- Solid materials that generate SO_2 upon thermal decomposition
- Chemical reactions that generate SO_2 quantitatively.

The advantages and disadvantages of each method are discussed in the following subsections.

Gas Cylinder Method

As an audit method for EPA Method 6, gas cylinders that contain SO_2 possess several advantages. The cylinders are easy to transport, handle, and use in the field, and they are commercially available at any required concentration. A major disadvantage is that use of a gas cylinder allows the analyst to inject a gas sample directly into an analyzer and determine the concentration in the cylinder. Also, verification of the manufacturer's concentration is necessary when a gas cylinder is purchased.

Permeation Tube Method

Permeation tube devices can be used to provide an accurately defined atmosphere and SO_2 permeation tubes are commercially available. These devices can be used almost indefinitely as long as the analyte remains in the tube. However, permeation tube devices require a dilution system and an apparatus to maintain the tube at a constant temperature (25° ± 0.1° C). Therefore, use of permeation tubes as an audit method would be difficult during field conditions.

Thermal Decomposition Method

Use of solid materials that quantitatively generate SO_2 upon thermal decomposition appears promising, especially in terms of field audit applications. Advantages of this method include:

- The required equipment is inexpensive, simply designed, and easy to transport to the field
- Temperature conditions required for the thermal decomposition of solids to generate SO_2 (probably ±5° C) are not as critical as those required for the permeation tube device.

The technique requires a Pyrex glass tube, a device for heating the tube (e.g., heating tape), a source of air, and a known amount of solid material. However, for such a system to be feasible the solid material must be stable at room temperature and must produce SO_2 quantitatively upon thermal decomposition.

Chemical Reaction Method

The use of solid-liquid reactions to generate SO_2 is widespread. The advantages of this method include:

- The required equipment is inexpensive, simply designed, and easy to transport to the field
- High temperatures generally are not required for chemical reactions.

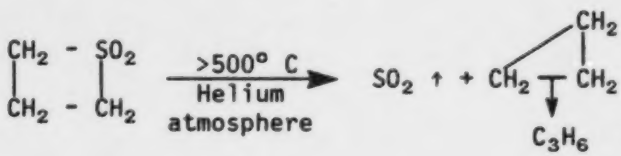
The technique requires a three-way, round-bottomed flask or an impinger; dilute sulfuric acid; and a known amount of solid material. However, for such a system to be feasible, the solid material must be stable at room temperature and must produce SO_2 quantitatively following a chemical reaction.

LABORATORY EVALUATION

Evaluation of the four audit systems that were considered for this study showed that gas cylinders and permeation tube devices have certain disadvantages. Hence, the last two approaches, thermal decomposition of solids and chemical reactions, were initially selected for evaluation in the laboratory.

Thermal Decomposition of Solids

A brief literature survey was performed to review suitable solid materials that meet the required criteria for thermal decomposition of solids. One category of species, sulfones, produces SO_2 when it is decomposed under specific temperature and pressure conditions. For example, Tsang et al. (1) studied the pyrolysis of trimethylene sulfone to generate dilute concentrations of SO_2. The reaction is:



Similarly, butadiene sulfone decomposes at about 200° C to generate SO_2 in the following reaction:

$$CH_2 - CH = CH - CH_2 - SO_2 \xrightarrow{<200^\circ\ C} SO_2 \uparrow + \text{olefin} \quad .$$

Compounds other than sulfones have been studied with respect to SO_2 generation. Benzothiophene dimerzes with the loss of SO_2 at 200° C with or without a solvent. Melamine sulfite decomposes thermally at 100° to 200° C to yield SO_2, melamines, and water vapor according to the following reaction (2):

$$(C_3H_6N_6)_2\ H_2SO_3 \cdot 4H_2O \xrightarrow{100^\circ\text{-}200^\circ\ C} 2\ C_3H_6N_6 + SO_2 \uparrow + 5H_2O \uparrow \quad .$$

RTI conducted preliminary experiments with trimethylene sulfone and butadiene sulfone. Trimethylene sulfone was used to generate SO_2 in the presence of air in the temperature range of 150° to 300° C. The SO_2 yield was <5 percent in this temperature range. Tsang et al. (1) reported that the reaction requires 500° C in a helium atmosphere for the quantitative decomposition of SO_2. Preliminary testing of butadiene sulfone generated a SO_2 yield of $\geq$50 percent at 150° C. Because a lower decomposition temperature

was desired for audit application in the field, further work using this approach was discontinued.

Chemical Reactions

The chemical reaction of sodium bisulfite or sodium sulfite with sulfuric acid to generate SO_2 is mentioned throughout the literature. Therefore, this reaction was evaluated in the laboratory for use as a field audit method for EPA Method 6. Preliminary experiments to generate SO_2 from the chemical reaction of sodium bisulfite and sulfuric acid were conducted using the experimental system shown in Figure 1. Initially, a known amount of sodium bisulfite was placed in a three-way, stoppered, round-bottomed glass flask, and dilute sulfuric acid (10 percent) was slowly added from a burette. Dry nitrogen or air was bubbled through the solution at a flow rate of 1 L/min to sweep the released SO_2 into a glass manifold. Glass wool was used to remove the aerosol vapors. The generated SO_2 was monitored continuously with a SO_2 source analyzer (TECO Model 40 fluorescent analyzer) to determine the complete reaction time. Within 10 min, the reaction was complete. In later experiments, the SO_2 gas generated from the chemical reaction was collected in an evacuated Tedlar bag. After 30 min of gas flow into the bag, the contents of the bag were diluted with zero air and analyzed for SO_2 using the source analyzer. The analyzer was calibrated with a known concentration of SO_2 in air. The experiments were repeated using various amounts of sodium bisulfite and different concentrations of sulfuric acid.

The measured SO_2 concentrations and the expected SO_2 concentrations from the stoichiometric chemical reaction are shown in Table 1. The results show that for various amounts of sodium bisulfite, the measured concentration of SO_2 ranged from 18 to 25 percent less than the expected SO_2 concentration from the stoichiometric reaction. The SO_2 generation was independent of flow rate (varied 0.1 to 1.4 L/min) and the amount of sulfuric acid when the sulfuric acid was slightly in excess of the amount required for completion of the reaction. The lower measured SO_2 concentrations were probably caused by the loss of SO_2 in the bag plus the loss of wet SO_2 on the glass system. However, the percent difference was constant within experimental error for various amounts of sodium bisulfite.

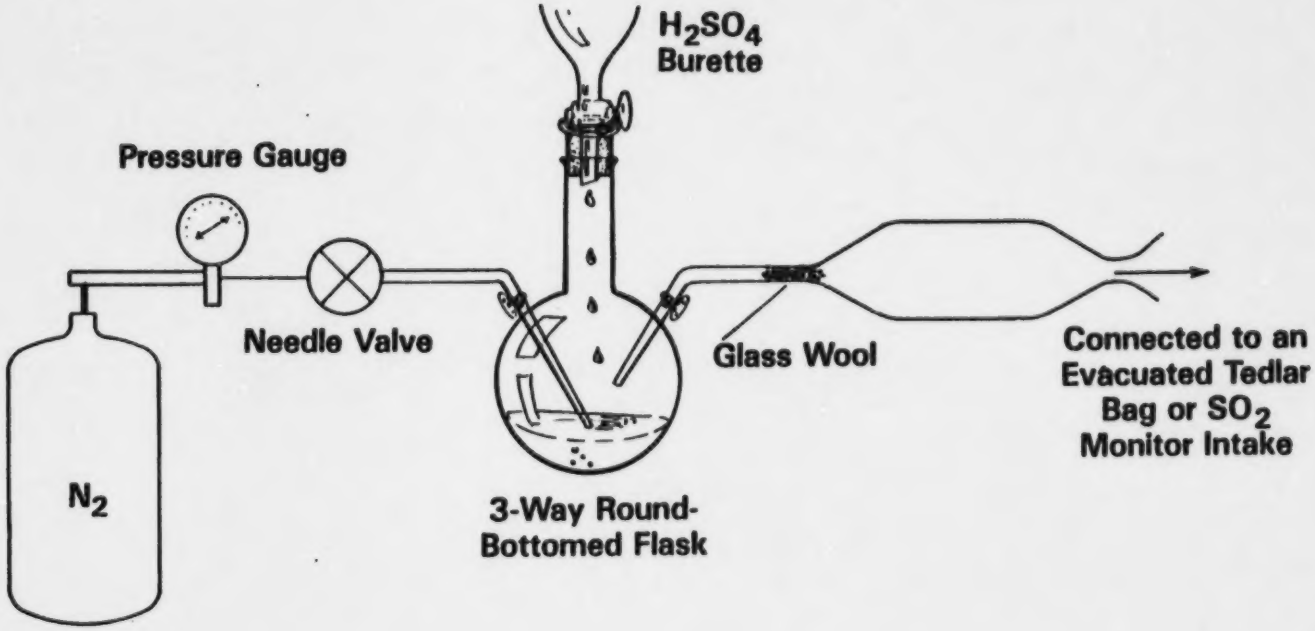


Figure 1. Preliminary SO_2 generation system.

TABLE 1. TEDLAR BAG RESULTS

Amount of $NaHSO_3$ (mg)	Expected SO_2 concentration[a] (ppm)	Measured SO_2 concentration (ppm)	Percent difference[b]
102.6	650	507	-21.9
199.9	804	646	-19.7
200.5	863	660	-23.5
200.6	801	604	-24.5
202.9	869	676	-22.2
201.4	799	652	-18.4
207.5	1,003	794	-20.8
202.3	842	712	-15.4
202.5	739	593	-19.8
401.9	944	721	-23.6

[a]Calculated from the stoichiometric chemical reaction.

[b]$$\text{Percent difference} = 100 \times \frac{\text{Measured } SO_2 \text{ concentrate} - \text{Expected } SO_2 \text{ concentrate}}{\text{Expected } SO_2 \text{ concentrate}}$$

AUDIT METHOD EVALUATION

The primary objective of this project was development of a simple method or device for evaluating the sampling and analytical phases of EPA Method 6. Therefore, experiments were performed using EPA Method 6 procedures as published in the Federal Register (see Appendix A). Except for the SO_2 gas generator, the sampling train component parts were the same as those in the EPA Method 6 train. The sampling probe was not required for this test. A modified midget impinger (Ace Glass, Inc., Model 7544-35) was used in place of a test site stack sample to generate a gas sample (SO_2) from the chemical reaction (Figure 2). While the SO_2 gas was being generated, it was drawn through the sampling train according to EPA Method 6 specifications and procedures. The preparation of tablets, SO_2 generation, and analysis procedures are described in the following subsections.

Preparation of Tablets

The developed method uses a known amount of sodium bisulfite or sodium sulfite to generate SO_2 quantitatively by reaction with 10-percent sulfuric acid. Because only a small amount of sodium bisulfite or sodium sulfite is required to generate source concentrations of SO_2 (~400 to 1,000 ppm), an inert binder (polyvinyl pyrollidine) was used for mixing. The mixture was formed into tablets or pills, which were made using either a potassium bromide die or a tablet press. The tablets or pills consisted of a layer of binder, a weighed amount of sodium bisulfite, and another layer of binder. A hydraulic press was used to apply several hundred pounds of pressure to form the tablet. The polyvinyl pyrollidine (PVP) binder is inert and water-soluble and, because the chemical compound is contained between the two layers of binder, the tablets can be handled safely. The binder also reduces the reaction rate of SO_2 generation. Tablets were made with varying amounts of sodium bisulfite to generate different concentrations of SO_2.

Sampling and Analysis Procedures

The step-by-step instructions for the generation and determination of SO_2 from the prepared tablets (quality assurance audit samples) are included in Appendix B. These procedures were followed in the laboratory evaluation

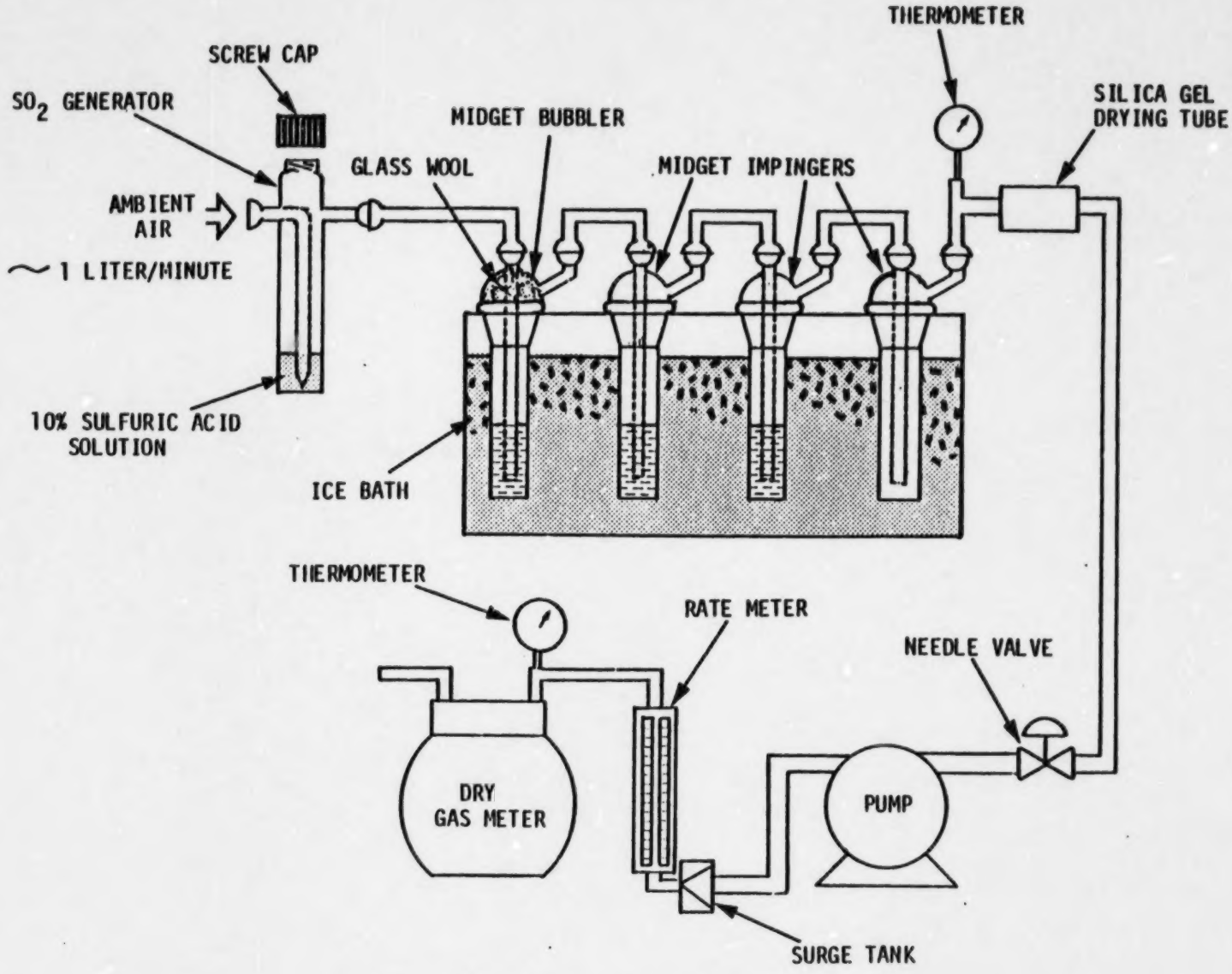


Figure 2. Sampling train with SO_2 generator.

experiments, except that the hydrogen peroxide impingers were analyzed by ion chromatography instead of colorimetric titration. Initial testing established that both analytical procedures give identical results.

Results and Discussion

The results obtained for different amounts of sodium bisulfite (ranging from 10 to 803 mg) are shown in Table 2. As these results indicate, the percent difference between the measured amount of SO_2 and the expected amount of SO_2 from the stoichiometric reaction ranged from 2 to 7 percent; i.e., SO_2 recoveries obtained were between 93 and 98 percent. Lower SO_2 recoveries were obtained for small amounts of sodium bisulfite (10 to 40 mg). Similar results were obtained for sodium sulfite. Sodium bisulfite was used for all the tests since small amounts are sufficient to generate required concentrations of SO_2. However, the SO_2 recoveries were poor for sodium metabisulfite. Blank runs (without a tablet) were performed, and results showed a negligible amount of SO_2. The flow rate, total volume of sample collection, and concentrations of sulfuric acid were varied, and the SO_2 generation from the material was found to be independent of these parameters. The amount of sulfuric acid needed must be slightly in excess of the amount stoichiometrically required.

STABILITY STUDY

A study was performed to determine the stability of the prepared tablets during a 6-month period at room temperature. The prepared tablets were analyzed periodically. The results of the stability study demonstrate that the tablets are stable within experimental error over the 6-month period (Table 3). The stability study is still in progress.

TABLE 2. RESULTS OF SO_2 GENERATED FROM THE PREPARED TABLETS[a] [b]

Weight of $NaHSO_3$ (mg)	Amount of SO_2 expected (mg)[c]	Amount of SO_2 measured (mg)	Percent difference[d]
12.9	7.9	5.2	-34.2
40.1	24.6	21.9	-11.0
50.6	31.1	31.3	+0.6
100.4	61.8	57.6	-6.8
101.6	62.5	61.5	-2.0
102.9	63.3	59.6	-5.8
202.9	124.9	120.3	-3.7
401.9	247.3	235.1	-2.0
802.3	493.7	464.4	-5.9
114.4[e]	38.5	23.9	-37.9
204.3[f]	103.8	105.1	+1.3

[a] Flow rate 1 L/min for 45 minutes.

[b] 3 to 5 mL of 10-percent H_2SO_4 added.

[c] Calculated from stoichiometric chemical reaction.

[d] $$\text{Percent difference} = 100 \times \frac{\text{Amount of } SO_2 \text{ measured} - \text{Amount of } SO_2 \text{ expected}}{\text{Amount of } SO_2 \text{ expected}}$$

[e] Sodium metabisulfite was used.

[f] Sodium sulfite was used.

TABLE 3. STABILITY STUDY RESULTS

Number of days	Amount of SO_2 expected (mg)	Amount of SO_2 measured (mg)	Percent difference[a]
0	122.7	121.9	-0.65
15	123.1	125.5	+1.95
29	123.0	124.9	+1.54
48	123.2	126.8	+2.90
68	121.7	124.4	+2.20
94	122.1	126.5	+3.55
180	121.5	125.3	+3.13

[a] $\text{Percent difference} = 100 \times \frac{\text{Amount of } SO_2 \text{ measured} - \text{Amount of } SO_2 \text{ expected}}{\text{Amount of } SO_2 \text{ expected}}$

SECTION 4
COLLABORATIVE TESTING

Another objective of this study was to determine the accuracy and precision of the developed method. The reliability of a method is best determined by collaborative testing, the traditional means used by EPA to establish intralaboratory and interlaboratory precision of a test method. During the test, a practical number of competent collaborators simultaneously analyze identical samples to determine the precision of the method and validate it for general use.

The accuracy of results obtained by a collaborative study is often more difficult to determine than the precision. However, in this study, the expected SO_2 concentrations from the stoichiometric reaction were compared to the average of measured SO_2 concentrations.

COLLABORATIVE TEST DESIGN

From the laboratories that have contracts with EPA, six were selected for the collaborative study based on their past experience in source testing. The laboratories were Engineering Science, Inc., Entropy Environmental, Inc., PEDCo Environmental, Inc., Radian Corporation, TRC-Environmental Consultants, Inc., and TRW-Environmental Engineering. Seven tablets representing two concentration levels were shipped to each laboratory for analyses to evaluate the feasibility of using the described method for auditing EPA Source Method 6 in the field. The true concentrations of the tablets were based on theoretical concentrations calculated from gravimetric preparations and the stoichiometric chemical reaction. Of the seven tablets, three had low concentrations (60 mg SO_2) and four had high concentrations (120 mg SO_2). A SO_2 generator (modified midget impinger), general instructions to perform the experiments, and a data sheet for reporting the results were also sent to each laboratory. The general instructions and a copy of the data sheet are included as Appendix B. Each laboratory was provided with

the true concentration for one tablet and was asked to analyze this tablet first; if the measured value was within ±10 percent, they analyzed the remaining six tablets. The trial run was necessary because most laboratories had not used this method and needed to become familiar with it. The laboratories were informed that these samples were not for an audit but only for an evaluation of the method and the types of compounds in the tablets were not disclosed. The laboratories were asked to report the results on the data sheet and to return the SO_2 generator.

INTERLABORATORY ANALYSIS RESULTS

The results of the analyses of the samples by the different laboratories and the expected concentrations are shown in Table 4. The analysis results usually agreed well with the expected values. For example, the average of the results of analyses of the low-concentration tablets ranged from -0.8 to +4.0 percent different from the expected value. Likewise, the average of the results of analyses of the high-concentration tablets ranged from -1.4 to +6.4 percent different from the average expected value. Two values reported from two laboratories were discarded during the statistical analysis because the laboratories identified problems during the SO_2 generation. Blank values reported by the laboratories were also negligible.

STATISTICAL ANALYSIS

The primary objective of the statistical analysis was to estimate the repeatability (or within-laboratory precision) and reproducibility (or between-laboratory precision) of the audit method developed for measuring SO_2. The repeatability is defined by Mandel[3] as the quantity that will be exceeded only about 5 percent of the time by the difference between two test results taken from the same laboratory on the same material. The reproducibility is defined similarly for the difference between two test results taken from different laboratories on the same material. It takes into account the repeatability as well as the effects of differences between laboratories and the effect of those laboratory differences changing from sample to sample.

The precision estimates were derived from the following linear model:

TABLE 4. INTERLABORATORY ANALYSIS RESULTS (mg)

	Known concentration	Low-concentration tablets			Percent difference[a]	High-concentration tablets			Percent (average)[a]
		1	2	3		1	2	3	
Lab 1									
RV	119.7	59.9	59.1	60.4	-0.8	119.0	119.9	122.6	-1.4
EV	121.8	60.3	60.4	60.3		122.2	122.3	122.1	
Lab 2									
RV	126.5	64.5	61.5	57.9	+1.7	129.4	128.0	131.7	+6.4
EV	122.2	60.3	60.2	60.4		122.0	121.8	121.9	
Lab 3		b							
RV	114.2		58.2	58.1	+4.0	118.7	115.8	115.6	-4.3
EV	122.2	-	60.7	60.7		121.9	122.1	122.0	
Lab 4									
RV	123.2	63.0	62.3	61.9	+3.1	128.4	124.9	125.6	+3.1
EV	122.7	60.5	60.4	60.5		122.4	122.6	122.5	
Lab 5									
RV	116.1	60.1	60.7	62.0	+1.3	116.7	119.6	120.5	-2.6
EV	121.8	59.9	60.0	60.3		122.1	122.1	122.2	
Lab 6			b						
RV	116.0	58.3		60.2	-2.6	117.0	118.0	118.0	-3.7
EV	122.4	60.9	-	60.8		122.4	122.3	122.3	

RV = Report value.

EV = Expected value.

[a]Percent difference = $\frac{\text{Average reported value - Average expected value}}{\text{Average expected value}} \times 100$.

[b]Values discarded.

$$Y = \mu + M + L + ML + E$$

where

Y = the SO_2 (mg) measurement
μ = the grand mean (a constant)
M = effect of levels (fixed at two levels)
L = effect of laboratories [random with variance V(L)]
ML = effect of interaction [random with variance V(ML)]
E = experimental error [random with variance V(E)].

The total variance associated with a measurement based on this model is:

$$V(Y) = V(L) + V(ML) + V(E),$$

where

$$\text{Repeatability} = \pm t \sqrt{2} \sqrt{V(E)}$$

$$\text{Reproducibility} = \pm t \sqrt{2} \sqrt{V(L) + V(ML) + V(E)} \quad .$$

The value t is a student t-value at the $\alpha = .05$ significance level for the appropriate degrees of freedom associated with the variance components. The interaction term is included in the reproducibility estimate to allow for the difference between laboratories changing from level to level. The model can also be defined on a level-by-level basis thus absorbing the interaction term into the between-laboratory variance component by estimating the components V(E) and V(L) for each separate level. The bias (a measure of accuracy) of the method is determined by the difference between the average value reported by the laboratories and the expected value based on stoichiometric reaction. The estimates of repeatability, reproducibility, and bias are summarized in Table 5. The mean concentrations of the expected and reported values for the low, high, and overall values are included in Table 5. The results indicate that the method can repeat measurements in a laboratory within ±5.0 mg about 95 percent of the time regardless of the concentration level.

Also, measurements by this method can be reproduced between laboratories within ±5.9 mg at the low concentration level or within ±23.8 mg at the high

TABLE 5. STATISTICAL ANALYSIS RESULTS[a] (mg)

	Tablets		
	Low concentration	High concentration	Overall
Reported SO_2 concentration	60.5	121.6	91.1
Expected SO_2 concentration	60.4	122.2	91.3
Repeatability[a] (within laboratory)	±5.2	±5.4	±5.0
Reproducibility[a] (between laboratories)	±5.9	±23.8	±12.7
Bias	0.1	0.6	0.2

[a]At 95-percent confidence limits.

concentration level about 95 percent of the time. The maximum bias observed was found to be 0.5 percent by comparison with the expected concentrations.

REFERENCES

1. Tsang, W., and Cornell, D. Pyrolysis generation of dilute concentration of sulfur dioxide. Anal. Chem., 46:933, 1974.

2. Gautney, J., Kim, Y. K., and Hatfield, J. B. Melamine: A regenerative SO_2 absorbent. J. Air Pollut. Control Assoc., 32:260-265, 1982.

3. Mandel, J. Repeatability and reproducibility. Materials Research and Standards, 11(8):8-16, 1971.

APPENDIX A
DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

METHOD 6

METHOD 6--DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

1. Principle and Applicability

1.1. Principle. A gas sample is extracted from the sampling point in the stack. The sulfuric acid mist (including sulfur trioxide) and the sulfur dioxide are separated. The sulfur dioxide fraction is measured by the barium-thorin titration method.

1.2 Applicability. This method is applicable for the determination of sulfur dioxide emissions from stationary sources. The minimum detectable limit of the method has been determined to be 3.4 milligrams (mg) of SO_2/m^3 (2.12×10^{-7} lb/ft^3). Although no upper limit has been established, tests have shown that concentrations as high as 80,000 mg/m^3 of SO_2 can be collected efficiently in two midget impingers, each containing 15 milliliters of 3 percent hydrogen peroxide, at a rate of 1.0 lpm for 20 minutes. Based on theoretical calculations, the upper concentration limit in a 20-liter sample is about 93,300 mg/m^3.

Possible interferents are free ammonia, water-soluble cations, and fluorides. The cations and fluorides are removed by glass wool filters and an isopropanol bubbler, and hence do not affect the SO_2 analysis. When samples are being taken from a gas stream with high concentrations of very fine metallic fumes (such as in inlets to control devices), a high-efficiency glass fiber filter must be used in place of the glass wool plug (i.e., the one in the probe) to remove the cation interferents.

Free ammonia interferes by reacting with SO_2 to form particulate sulfite and by reacting with the indicator. If free ammonia is

present (this can be determined by knowledge of the process and noticing white particulate matter in the probe and isopropanol bubbler), alternative methods, subject to the approval of the Administrator, U. S. Environmental Protection Agency, are required.

2. Apparatus

2.1 Sampling. The sampling train is shown in Figure 6-1, and component parts are discussed below. The tester has the option of substituting sampling equipment described in Method 8 in place of the midget impinger equipment of Method 6. However, the Method 8 train must be modified to include a heated filter between the probe and isopropanol impinger, and the operation of the sampling train and sample analysis must be at the flow rates and solution volumes defined in Method 8.

The tester also has the option of determining SO_2 simultaneously with particulate matter and moisture determinations by (1) replacing the water in a Method 5 impinger system with 3 percent peroxide solution, or (2) by replacing the Method 5 water impinger system with a Method 8 isopropanol-filter-peroxide system. The analysis for SO_2 must be consistent with the procedure in Method 8.

2.1.1 Probe. Borosilicate glass, or stainless steel (other materials of construction may be used, subject to the approval of the Administrator), approximately 6-mm inside diameter, with a heating system to prevent water condensation and a filter (either in-stack or heated out-stack) to remove particulate matter, including sulfuric acid mist. A plug of glass wool is a satisfactory filter.

2.1.2 Bubbler and Impingers. One midget bubbler, with medium-coarse glass frit and borosilicate or quartz glass wool

2.1.7 Valve. Needle valve, to regulate sample gas flow rate.

2.1.8 Pump. Leak-free diaphragm pump, or equivalent, to pull gas through the train. Install a small surge tank between the pump and rate meter to eliminate the pulsation effect of the diaphragm pump on the rotameter.

2.1.9 Rate Meter. Rotameter, or equivalent, capable of measuring flow rate to within 2 percent of the selected flow rate of about 1000 cc/min.

2.1.10 Volume Meter. Dry gas meter, sufficiently accurate to measure the sample volume within 2 percent, calibrated at the selected flow rate and conditions actually encountered during sampling, and equipped with a temperature gauge (dial thermometer, or equivalent) capable of measuring temperature to within 3°C (5.4°F).

2.1.11 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby national weather service station, in which case the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase or vice versa for elevation decrease.

the $KMnO_4$ test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

3.1.2 Isopropanol, 80 percent. Mix 80 ml of isopropanol with 20 ml of deionized, distilled water. Check each lot of isopropanol for peroxide impurities as follows: shake 10 ml of isopropanol with 10 ml of freshly prepared 10 percent potassium iodide solution. Prepare a blank by similarly treating 10 ml of distilled water. After 1 minute, read the absorbance at 352 nanometers on a spectrophotometer (Note: Use a 1-cm path length). If absorbance exceeds 0.1, reject alcohol for use.

Peroxides may be removed from isopropanol by redistilling or by passage through a column of activated alumina; however, reagent grade isopropanol with suitably low peroxide levels may be obtained from commercial sources. Rejection of contaminated lots may, therefore, be a more efficient procedure.

3.1.3 Hydrogen Peroxide, 3 Percent. Dilute 30 percent hydrogen peroxide 1:9 (v/v) with deionized, distilled water (30 ml is needed per sample). Prepare fresh daily.

3.1.4 Potassium Iodide Solution, 10 Percent. Dissolve 10.0 grams KI in deionized, distilled water and dilute to 100 ml. Prepare when needed.

3.2 Sample Recovery.

3.2.1 Water. Deionized, distilled, as in 3.1.1.

3.2.2 Isopropanol, 80 Percent. Mix 80 ml of isopropanol with 20 ml of deionized, distilled water.

Temporarily attach a suitable (e.g., 0-40 cc/min) rotameter to the outlet of the dry gas meter and place a vacuum gauge at or near the probe inlet. Plug the probe inlet, pull a vacuum of at least 250 mm Hg (10 in. Hg), and note the flow rate as indicated by the rotameter. A leakage rate not in excess of 2 percent of the average sampling rate is acceptable. Note: Carefully release the probe inlet plug before turning off the pump.

It is suggested (not mandatory) that the pump be leak-checked separately, either prior to or after the sampling run. If done prior to the sampling run, the pump leak-check shall precede the leak check of the sampling train described immediately above; if done after the sampling run, the pump leak-check shall follow the train leak-check. To leak check the pump, proceed as follows: Disconnect the drying tube from the probe-impinger assembly. Place a vacuum gauge at the inlet to either the drying tube or the pump, pull a vacuum of 250 mm (10 in.) Hg, plug or pinch off the outlet of the flow meter and then turn off the pump. The vacuum should remain stable for at least 30 seconds.

Other leak-check procedures may be used, subject to the approval of the Administrator, U.S. Environmental Protection Agency.

4.2 Sample Recovery. Disconnect the impingers after purging. Discard the contents of the midget bubbler. Pour the contents of the midget impingers into a leak-free polyethylene bottle for shipment. Rinse the three midget impingers and the connecting tubes with deionized, distilled water, and add the washings to the same storage container. Mark the fluid level. Seal and identify the sample container.

4.3 Sample Analysis. Note level of liquid in container, and confirm whether any sample was lost during shipment; note this on analytical data sheet. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results.

Transfer the contents of the storage container to a 100-ml volumetric flask and dilute to exactly 100 ml with deionized, distilled water. Pipette a 20-ml aliquot of this solution into a 250-ml Erlenmeyer flask, add 80 ml of 100 percent isopropanol and two to four drops of thorin indicator, and titrate to a pink endpoint using 0.0100 N barium perchlorate. Repeat and average the titration volumes. Run a blank with each series of samples. Replicate titrations must agree within 1 percent or 0.2 ml, whichever is larger.

(Note: Protect the 0.0100 N barium perchlorate solution from evaporation at all times.)

not deviate by more than 5 percent from the initial calibration factor (determined in Section 5.1.1), then the dry gas meter volumes obtained during the test series are acceptable. If the calibration factor deviates by more than 5 percent, recalibrate the metering system as in Section 5.1.1, and for the calculations, use the calibration factor (initial or recalibration) that yields the lower gas volume for each test run.

5.2 Thermometers. Calibrate against mercury-in-glass thermometers.

5.3 Rotameter. The rotameter need not be calibrated, but should be cleaned and maintained according to the manufacturer's instruction.

5.4 Barometer. Calibrate against a mercury barometer.

5.5 Barium Perchlorate Solution. Standardize the barium perchlorate solution against 25 ml of standard sulfuric acid to which 100 ml of 100 percent isopropanol has been added.

6. Calculations

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculation.

6.1 Nomenclature.

C_{SO_2} = Concentration of sulfur dioxide, dry basis corrected to standard conditions, mg/dscm (lb/dscf).

N = Normality of barium perchlorate titrant, milliequivalents/ml.

P_{bar} = Barometric pressure at the exit orifice of the dry gas meter, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

T_m = Average dry gas meter absolute temperature, °K (°R).

T_{std} = Standard absolute temperature, 293° K (528° R).

7. Bibliography

1. Atmospheric Emissions from Sulfuric Acid Manufacturing Processes. U.S. DHEW, PHS, Division of Air Pollution. Public Health Service Publication No. 999-AP-13. Cincinnati, Ohio. 1965.

2. Corbett, P.F. The Determination of SO_2 and SO_3 in Flue Gases. Journal of the Institute of Fuel. 24:237-243, 1961.

3. Matty, R. E. and E. K. Diehl. Measuring Flue-Gas SO_2 and SO_3. Power. 101:94-97. November 1957.

4. Patton, W. F. and J. A. Brink, Jr. New Equipment and Techniques for Sampling Chemical Process Gases. J. Air Pollution Control Association. 13:162. 1963.

5. Rom, J. J. Maintenance, Calibration, and Operation of Isokinetic Source-Sampling Equipment. Office of Air Programs, Environmental Protection Agency. Research Triangle Park, N. C. APTD-0576. March 1972.

6. Hamil, H. F. and D. E. Camann. Collaborative Study of Method for the Determination of Sulfur Dioxide Emissions From Stationary Sources (Fossil-Fuel Fired Steam Generators). Environmental Protection Agency, Research Triangle Park, N. C. EPA-650/4-74-024. December 1973.

7. Annual Book of ASTM Standards. Part 31; Water, Atmospheric Analysis. American Society for Testing and Materials. Philadelphia, PA. 1974. pp. 40-42.

8. Knoll, J. E. and M. R. Midgett. The Application of EPA Method 6 to High Sulfur Dioxide Concentrations. Environmental Protection Agency. Research Triangle Park, N. C. EPA-600/4-76-038. July 1976.

APPENDIX B
OUTLINE OF METHOD 6 AUDIT PROCEDURE

OUTLINE OF METHOD 6 AUDIT PROCEDURE

(1) Obtain special tablets from EPA.

One known concentration
Six unknown concentrations

(2) Set up apparatus as shown in Figure 1 (generator and EPA Method 6 Sampling Train).

(3) Check for leaks according to attached instructions.

(4) Generate the known SO_2 concentration according to the attached instructions.

(5) Analyze the collected solutions by EPA Method 6 and calculate the results.

(6) If the result from the known tablet is within ±10% of the expected value, proceed in the same manner with the unknowns. If not, call Dr. Jayanty (919/541-6483), Research Triangle Institute, Research Triangle Park, NC, to discuss possible problems.

(7) Generate and analyze the six remaining concentrations and calculate the results.

(8) Record the results on the attached record sheet and send them to:

U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Quality Assurance Division (MD-77)
Research Triangle Park, NC 27711

ATTN: Robert G. Fuerst

INSTRUCTIONS FOR THE GENERATION AND DETERMINATION OF SULFUR DIOXIDE FROM QUALITY ASSURANCE AUDIT SAMPLES

1. Principle

1.1 A gas sample (sulfur dioxide) is generated from a chemical reaction in a modified Midget impinger and is used in place of the test site stack sample. While the SO_2 gas is being generated, it is drawn through an EPA Method 6 SO_2 sampling train according to EPA Method 6 specifications and procedure. The sulfuric acid mist (including sulfur trioxide) and the sulfur dioxide are separated. The sulfur dioxide fraction is measured by the barium thorin titration method (EPA Method 6 procedure).

2. Apparatus

2.1 Sampling. The sampling train, including the SO_2 gas generator, is shown in Figure 1. The sampling train component parts, except the SO_2 gas generator, are the same as those used for EPA Method 6. The sampling probe is not required; therefore, it is not included in the train.

2.1.1 SO_2 gas generator: Modified Midget impinger (Ace Glass, Inc., Model 7544-35) is supplied. The generator must be connected to the sampling train with leak-free glass connectors. Silicone grease may be used, if necessary, to prevent leakage.

2.2 Sample Recovery

Refer to EPA Method 6, Section 2.2.

2.3 Analysis

Refer to EPA Method 6, Section 2.3.

3. Reagents

3.1 Audit Material (Pills): The audit material is supplied in the form of pills. Only one pill is to be used for each test run. The pills must be handled carefully and added to the generator with clean tweezers without breaking or crumbling the pill. Record which pill number is being used for each run.

3.2 10-percent sulfuric acid: 10 ml of concentrated sulfuric acid diluted with deionized water in a 100-ml volumetric flask.

3.3 All other reagents and their specifications should be followed as listed in Section 3 of EPA Method 6.

4. Procedure

4.1 Sampling

4.1.1 Preparation of SO_2 sampling train: Measure 10 ml of 10-percent sulfuric acid solution into the supplied SO_2 generator. Measure 15 ml of 80-percent isopropanol into the midget bubbler and 15 ml of 3-percent hydrogen peroxide into each of the first two midget impingers. Leave the final midget impinger dry. Assemble the train as shown in Figure 1. Place crushed ice and water around the impingers but not around the SO_2 generator.

4.1.2 Leak-check procedure. Before the sampling run, check for leaks without adding acid to the SO_2 generator. Set up the sampling train as shown in Figure 1 without the acid in the generator and follow the leak check procedure described in Section 4.1.2 of EPA Method 6. During sampling, visually examine all glass connections.

4.1.3 Sample generation. Remove the SO_2 generator screw cap and start the pump. The flow rate (1 l/min) is the same as that for EPA Method 6. Hold the cap in one hand, carefully drop a pill (audit material supplied) into sulfuric acid solution while the pump is still running. Then, immediately (within a few seconds) replace and securely tighten the screw cap. Start a stopwatch after dropping the pill.

4.2 Sample Collection. Follow the sample collection procedure in Section 4.1.3 of EPA Method 6 except for the following modifications. The gas sample is drawn from the SO_2 generator for 45 minutes. The pill generally takes 25 minutes to dissolve completely; however, continue the sample collection for another 20 minutes.

NOTE: Ambient air is used to draw the sample from the generator. Hence, ambient air must be free of sulfur dioxide. To test ambient air, perform a blank run (without a pill) for 45 minutes and analyze impinger solutions. Analysis results should indicate a negligible amount of sulfur dioxide.

4.3 Sample Recovery. Follow the procedures described in Section 4.2 of EPA Method 6. In addition, discard the contents from the SO_2 generator and clean the generator for the next run.

4.4 Sample Analysis. Follow EPA Method 6 procedures (Sections 4.3, 5, and 6) for sample analysis, calibration, and calculations. Report the amount of SO_2 recovered in milligrams and the gas volume in dry standard cubic meters or dry standard cubic feet on the data sheet.

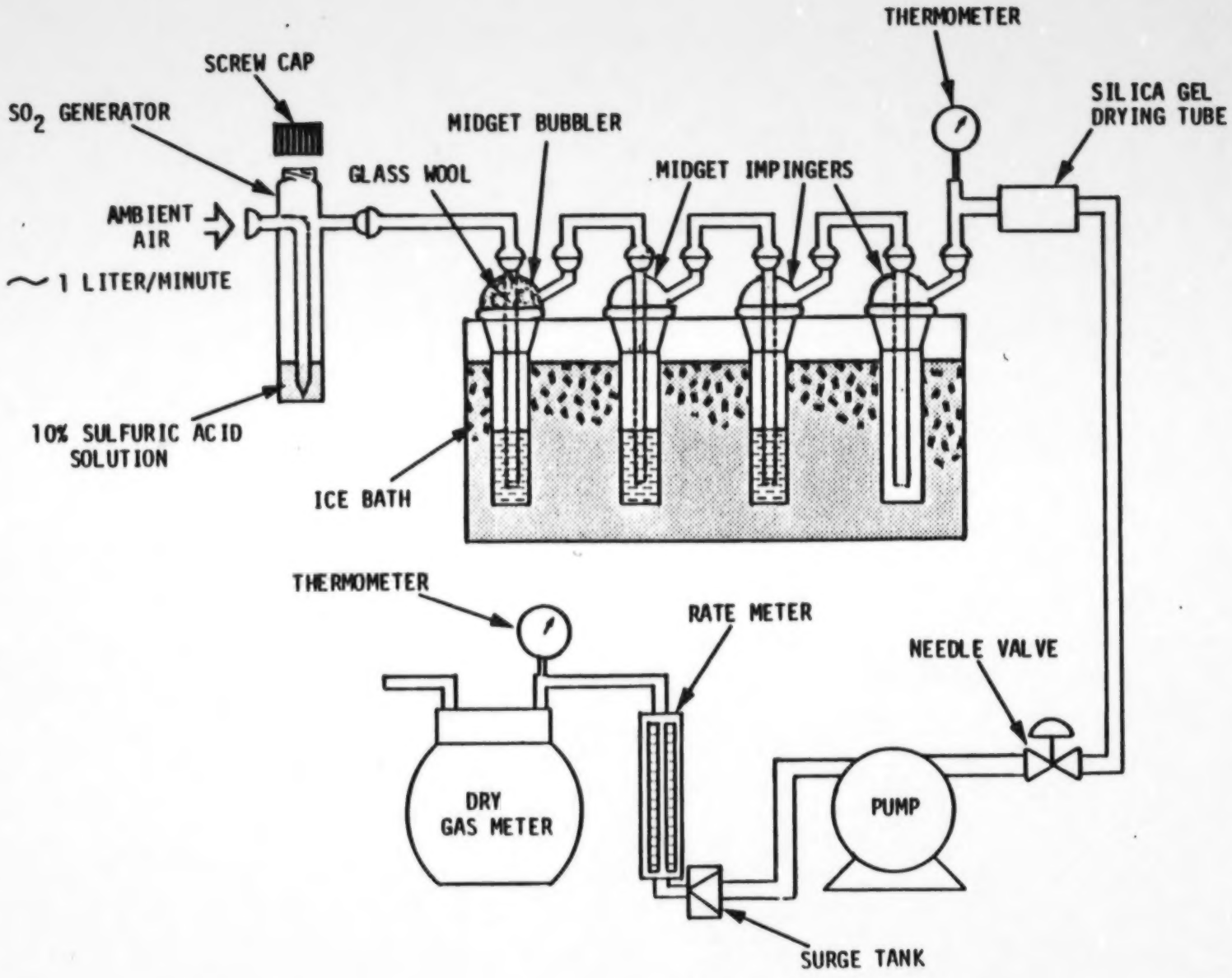


Figure 1: SO_2 Sampling Train With SO_2 Generator

DATA SHEET

LAB NAME:

ANALYST NAME:

	SAMPLE NUMBERS						
	KNOWN						
Normality							
Aliquot vol							
Titrant vol							
Blank vol							
Solution vol							
mg SO_2							
Gas vol							

Please return data sheet to:

Mr. Robert G. Fuerst
Environmental Protection Agency
EMSL/QAD MD-77
Research Triangle Park, NC 27711